Assistance Agreement Quarterly Report Summary: 12th Quarter

Date of Report: February 5, 2003

Agreement No: R82806301

Title: **Baltimore Supersite: Highly Time and Size Resolved Concentrations of Urban PM2.5 and its Constituents for Resolution of Sources and Immune Responses**

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Institution: Department of Chemistry and Biochemistry, University of Maryland, College Park, MD

Research Category: Particulate Matter Supersites Program

Project Period: January 15, 2000 to December 31, 2003

Objectives of Research: Our primary objectives are to I) provide an extended, ultra high-quality multivariate data set, with unprecedented temporal resolution, designed to take maximum advantage of advanced new factor analysis and state-of-the-art multivariate statistical techniques; ii) provide important information on the potential for health effects of particles from specific sources and generic types of sources, iii) provide large quantities of well characterized urban PM for retrospective chemical, physical, biologic analyses and toxicological testing, iv) provide sorely needed data on the sources and nature of organic aerosol presently unavailable for the region, v) provide support to existing exposure and epidemiologic studies to achieve enhanced evaluation of health outcome-pollutant and -source relationships, and vi) test the specific hypothesis listed in our proposal.

ACTIVITIES
During the 12th report period the following activities were performed.
    1. Completed operation of the Ponca St. Site, including the November 2002 intensive
    2. Presentations were made at the Fall EPA meeting in Atlanta
    3. Quality assurance, database loading, and preparations for transferring data to the NARSTO data base are in progress.

Status of data reduction, QA, loading to the Baltimore Supersite, and transfer of data to the NARSTO archive and Supersites Relational Database are discussed below.

STATUS

LIDAR

Due to both lasers breaking on September 13, the Lidar was non operational for the weekly sampling. The lasers were sent to BigSkyLaser for Repair and were returned in December. However, sampling could not be restarted in December due to low temperatures. The electronics malfunction for temperatures lower than 5º C. The determination of the Atmospheric Boundary Layer height from lidar data of the entire supersite experiment is close to completion.

In the near future we will compute the aerosol vertical extinction coefficient for all periods. The vertical profile of the particle size distribution could then be computed through an inversion of the extinction equation. In a subsequent step we expect to be able to infer details on the chemical composition of the atmosphere by means of the refractive index. A publication on this topic is under preparation.

METEOROLOGICAL DATA

Data was sampled continuously during the entire time period. Plots of 5 minute averages are available online at http://www.jhu.edu/~dogee/mbp/supersite2001/. The instrumentation and periods of missing data are listed in the table below.

Date/time when lidar was running

date	time	comments
3-Jul	10.26 - 19.30	
4-Jul	8.43 - 18.50	
5-Jul	7.50 - 19.15	
6-Jul	8.32 - 18.15	
7-Jul	7.51 - 19.37	
8-Jul	8.01 - 18.34	
9-Jul	11.27 - 18.34	
10-Jul	8.33 - 18.31	
11-Jul	8.24 - 18.21	
12-Jul	13.10 - 17.47	
13-Jul	8.20 - 18.27	
14-Jul		rainy
15-Jul	9.01 - 18.18	
16-Jul	8.21 - 18.24	
17-Jul	10.39 - 12.30	lidar taken out
18-Jul	11.11 - 17.09	
19-Jul		lidar taken out
20-Jul	8.28 - 18.34	
21-Jul	8.44 - 19.42	
22-Jul	8.55 - 18.35	

With respect to data quality all sensors operated within errors specified by the manufacturer. Solar radiation, mean wind speeds, temperature and humidity showed the expected diurnal variations. Moreover, turbulence parameters such as atmospheric stability and friction velocity showed corresponding behavior. The turbulence sensor (3d sonic anemometer) does not collect data when its surface is wet. Long and frequent rain events during September - December resulted in gaps in the data. Overall Met data availability was 94.7%.

NEPHELOMETERS

Both nephelometers worked fine during this period.

DATA REDUCTION, CORRECTIONS, AND VALIDATIONS

Procedure. In the BSS project data from all instruments operated by the University of Maryland were captured to the site server computer and uploaded to the BSS database machine for storage. The stored data, including all recorded instrument parameters, were then loaded into the BSS SQL relational database, for inspection and further processing. After loading, an instrument parameter flagging application is run to flag the data as good, bad, or correctable based on the values of instrument parameters and status codes, according to protocols which we have established. The data are then flagged using an operator log flagging application. This allows us to flag data which appear to be valid based on instrument parameters, but which the operators know to be invalid, e.g., when filters or flow monitoring devices are temporarily placed on inlets for calibration or auditing purposes. As necessary, calibration corrections (i.e., span gas audit corrections and conversion efficiency factors) and recalculations are applied. Some of these arose from faulty or in appropriate algorithms inherent to the manufacturer's software/instrument control system. For example, atmospheric concentrations reported by our R&P instruments (i.e., R&P TEOM, R&P 8400N, R&P 8400S, and R&P 2100) are referenced to 25°C, not ambient temperature as prescribed by EPA. Likewise the TEOM PM2.5 reported data after multiplying by 1.03 and adding 3 $\mu g/m^3$. We elected to implement recalculations, audit and efficiency corrections, and adjustments to ambient temperature by building database applications run by the Data Manger, because of the likelihood that some corrections might change once the entire data sets were examined and because implementation of such changes could be centrally managed more easily and rigorously documented in this manner.

Our goal is to produce Level II data as required by EPA for the NARSTO archive. Level II data protocol requires that data are checked for "reasonableness" (including mass balance and out-of-range considerations) and comparison with reference methods. Out of range values are flagged by the instrument parameter flagging function. Mass balance checks can only be done after the measurements for all of the species have been adequately processed and only after the reference data are obtained. Reference methods for PM2.5 mass and component species (Sulfate, Nitrate, EC, OC) are the 24-hr FRM PM2.5 and Speciation Monitor data.

Once data reach Level II quality, they are to be delivered to Clarkson University who will convert the data to NARSTO format and submit it to the NARSTO archive. As Level II requires a reasonableness check based on mass balance, Sulfate, Nitrate, and ECOC data cannot be released until data reduction for all of these instruments has been completed.

The status of data loading, flagging, corrections, and recalculations, are presented below.

MET DATA: Meterological data have all been loaded into the BSS database. Flagging was done prior to loading by Johns Hopkins University. These data are being sent to Clarkson University for entry into the NARSTO archival format.

APS:SMPS: All data collected at Ponca St. with the Aerodynamic Particle and Scanning Mobility Particle Sizers have been loaded into the BSS data base both instrument and operator flagging has been completed. These data are ready to submit to Clarkson for the NARSTO

archive.

TEOM: All BSS TEOM data have been loaded in to BSSDB and both instrument and operator log flagging applications have been implemented. Additionally, we have corrected the data to undo the manufacturer's algorithm, which transformed all data to what we understand is an estimate of the PM10 concentration and we have corrected the instrument start times for various periods due to errors in the manufacturer's software and clock drift problems. All data are now temperature and pressure corrected to reflect ambient outdoor conditions at the time of measurement. The TEOM PM2.5 have been compared with Speciation sampler PM2.5 data, which they well agree. Comparisons for Ponca St. TEOM and Speciation monitor PM2.5 mass data are shown in the Figure to the right. The average deviation between these measurements is 0.81 $\mu g/m^3$. Validated FRM PM2.5 data have not yet been received.

Figure 1a. Time series plots

$$y = 1.0753x - 2.3159$$
$$R^2 = 0.9543$$

NITRATE: The R&P 8400N semicontinuous Nitrate Monitor was used at Clifton Park as well as Ponca St. All data from both sites have been loaded into the BSS data base. Instrument parameter and operator log flagging applications have been run. Final Audit correction and Conversion Efficiency Factors have been calculated and applied to all Ponca St. and Clifton Data. Additionally, we have developed a function characterizing the effect of deviations of the instrument's reaction cell temperature and implemented this correction also. Despite these corrections, 24 hr averages of the semicontinuous Nitrate data are typically 48% less than the 24-hr speciation monitor data for the same time period. As indicated in the
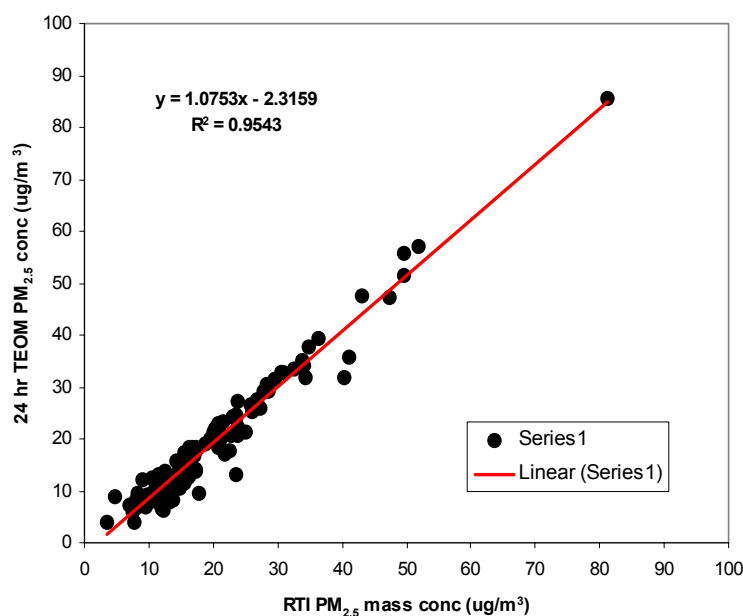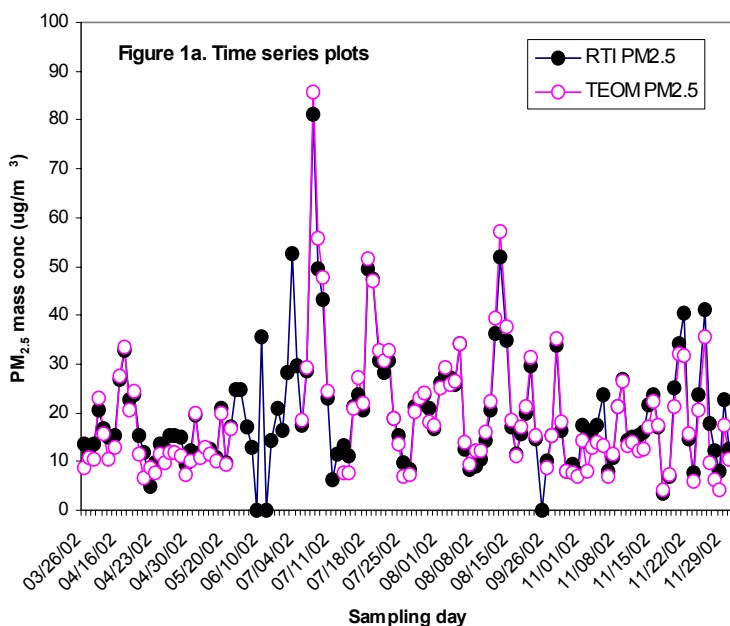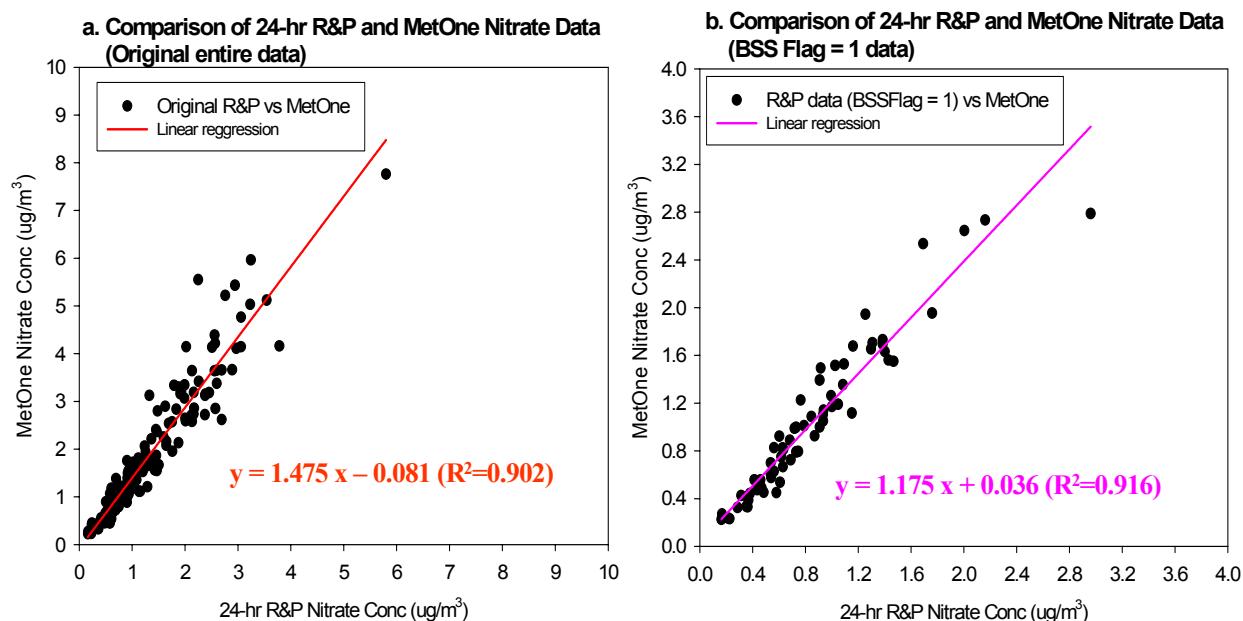
Figure below, this difference was only 17% for data for which the BSS flag was equal to 1, i.e., good. Examination of the data show that large deviations were observed when the ambient outdoor temperatures were much cooler than the indoor temperature, as has been previously reported.   We are endeavoring to develop a correction algorithm to reduce this difference. This is especially important as the Harvard Sulfate data collected at the Ponca St. site require a correction for particulate Nitrate.

Comparison of Original R&P and MetOne Nitrate Data (Baltimore UMCP Data)

a. Comparison of 24-hr R&P and MetOne Nitrate Data (Original entire data)

$y = 1.475\ x - 0.081\ (R^2=0.902)$

b. Comparison of 24-hr R&P and MetOne Nitrate Data (BSS Flag = 1 data)

$y = 1.175\ x + 0.036\ (R^2=0.916)$

~48% negative bias in Baltimore nitrate data

SULFATE: Sulfate was measured at 10 minute intervals at Clifton Park with the R&P 8400 S Sulfate Monitor.   At Ponca st. we used a Harvard-style sulfate instrument in which sulfate is converted to SO_2 and the SO_2 measured continuously while a solenoid valve is actuated to provide filtered (background) between successive measurements of sample air. While the timing of these periods is know, residence time in the instrument result in an exponential decay of the signal with a time constant that depends on the magnitude of the SO_2 signal.   Because of the substantial variability in sulfate (and hence measured SO_2 concentrations) the data reduction algorithm could not, therefore, use strict interval timing for peak integration and background correction. We have now developed and tested a data reduction algorithm which is not sensitive to sulfate concentration excursions, while still maximizing the information contained in the background and sampling intervals.   All raw data collected at Ponca St. with this instrument have been loaded in to the BSS database and have now been reduced. Most of the Ponca St.

Data have been flagged, however, flagging remains to be done on the earlier data collected at Ponca St. Span gas audit correction factors have been developed. Currently, corrections for particle Nitrate, and in the earlier data (prior to application of a carbon monolith denuder), NOx must be applied. After flagging and application of nitrate/NOx corrections, the instrument efficiency factor will be evaluated by comparing 24-hr averages with integral 24-hr speciation measurements.

ECOC. Raw ECOC data collected at Ponca St. with the Sunset Labs field instrument have been analyzed. The operator flagging log has been prepared for the flagging application and needs to be implemented. We are awaiting some final definitive calibration data from Sunset labs, and having gone through thousands of records carefully, approximately 300 require reanalysis due to instrument problems. ECOC data collected with the R&P 2100 ECOC instrument

SEAS: All SEAS instrument data have been loaded into the BSS database. The Instrument parameter flagging application has been run. Approximately 1200 SEAS slurry samples will be analyzed off-line by atomic absorption spectrometry. As this represents only about 10% of those collected, samples are being selected on the basis of wind angle in relation to known sources, sample validity, and availability of data from the other instruments. Approximately 350 analyses have been completed to date. Several hundred samples from the July 2002 intensive have been selected for Metals and Cytokine analyses and are being processed. This will take several months. Choosing which samples to analyze depends on which other data we have and requires time-consuming checks of records for all instruments. Don't expect SEAS data to be in the Narsto archive for at least another 6 months - probably end of summer.

SEQUENTIAL ORGANIC SAMPLER DATA: Major and Minor flow rates and Date/time stamps were the only data logged continuously for this instrument. These data have been appropriately reduced and entered into the operator log (a spreadsheet file).

OTHER DATA: The following data sets need to be loaded into BSSDB: Nephelometer data, FRM and Speciation data, SEAS metals concentration data, SEAS Cytokine response data (not yet existent) , Organic Compound analysis data, Single Particle MS data (not yet received), Traffic data (traffic tunnels and data for streets adjacent to the site), Drum impactor synchrotron XRF data (not yet received), VOC-online GC, O3, NOx, CO, and VOC canister data.

SUPERSITES RELATIONAL DATABASE

A total o f 399 Mb of data have been received from the EPA Supersites. !.5 Gb of Speciation Monitoring Network data have been received for the period June - September, 2001. In addition 117 MB have been received from the SEARCH, 0.11 MB from TVA, 4.9 MB from Boston PM Center, and 3.25 MB of airway data from the National Climatic Data Center.

PUBLICATIONS

Mitkus, RJ, Falconer, MO, Powell, JL, Ondov, JM and KS Squibb. In vitro assay of the biological activity of ambient PM2.5 collected by a high frequency aerosol sampler. The Toxicologist 66: 359, 2002.

PRESENTATIONS/MEETINGS

AGS Meeting, San Francisco, December, 2002

1.   Adam, M., Pahlow, M., Ondov, J., Thomas, M., Parlange, M. (2002) Atmospheric boundary layer extinction coefficient from the 2001/2002 Baltimore PM Supersite experiments. Presented at the Fall meeting of the American Geophysical Society, Dec. 6-7, San Francisco. Poster: A52C-0125

AAAR Meeting, Charlotte, October, 2002

2.   SONG, X.-H., Hopke, P. K., Paatero, P., Ondov, J. M., Kidwell, C. B. (2002). Source Identification by a Multilinear Receptor Model Using Highly Time Resolved Chemical Composition and Wind Data. Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.

3.   Ondov, J. M. (2002) Highly Time and Size Resolved Concentrations of Urban Pm2.5 and its Constituents for Resolution of Sources and Immune Responses: Highlights of Results from the Baltimore Supersite Project." Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.

4.   Harrison, D., Nair, N., Park, S. S., Pancras, J. P., Gazula, S., Ondov, J. M. (2002) Resolution of a Municipal Diesel Emission Component at the Baltimore Supersite from Highly Time- and Compositionally-resolved Aerosol and Gas. Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.

5.   Mitkus R., Squibb[1], K., Powell, J., Catino, D. H., Ondov, J. M. (2002). In Vitro Assay of the Biological Activity of $Pm_{2.5}$ and its Components Collected by a High Frequency Aerosol Sampler at an Urban Supersite. Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.

6.   Park, S. S., Pancras, P., Chang, Y. C., Catino, D. H., Gazula, S., Ondov, J. M. Seung S. Park, Patrick Pancras, Yu Chen Chang, Dawn H. Cation, and S. (2002) Investigation of Sources with Highly Time-resolved Aerosol at the Baltimore Supersite Using Positive Matrix Factorization   Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.

7.　　Pancras, J. P., Gazula, S., Park, S. S., Ondov, J. M., Stevens, R. K. (2002) Elemental and Inorganic Analysis of Highly-time-resolved Aerosol Constituents in the Tampa Bay Regional Atmospheric Chemistry Experiment (BRACE) Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.

8.　　Park, S. S., Pancras, J. P., Gazula, S., Ondov, J. M. (2002) Sources of Elemental Aerosol Constituents in Pittsburgh Using Positive Matrix Factorization of Highly Time-resolved DataTo be presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.

9.　　Wolfgang F. Rogge, Orhan Sevimoglu, Anna Bernardo-Bricker, Yu Chen Chang, David Harrison Organic PM2.5 at the Baltimore PM Supersite: Diurnal Variation with a Resolution of Three Hours. Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.

10.　Markus Pahlow, Jan Kleissl, Marc B. Parlange, John M. Ondov and David Harrison, "Characteristics of the Atmospheric Boundary Layer as observed During the Baltimore PM Supersite Experiment"Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.

EGS-AGU, 2003

11.　Adam, M.; Pahlow, M.; Kovalev, V.; Ondov, J.; Balin, I.; Simeonov, V.; van den Bergh, H.; Parlange, M. Determination of the Vertical Extinction Coefficient Profile in the Atmospheric Boundary Layer and the Free Troposphere" To be presented at EGS-AGU, 6-12 April 2003, Nice, France

12.　Mariana Adam, Markus Pahlow, Marc Parlange, John Ondov, "Atmospheric Boundary Layer characterization during the Baltimore PM Supersite - July 2002" AAAR, 31 March - 4 April 2003, Pittsburgh, PA
P11-16

Society of Toxicology Meeting, March 2003

R Mitkus, J Powell, M Akkerman and K Squibb. Differential Immunological Response of Two Airway Cell Types to Zinc (Zn), an Active Component of Urban Particulate Mattter (PM). To be presented at the Society of Toxicology annual meeting, March 9-13, 2003.

AAAR Meeting, March 2003
R. Mitkus, J. Powell, M. Akkerman, J. Ondov and K. Squibb. Cytokine responses elicited by PM2.5 SEAS samples collected at the Baltimore Supersite during a 2002 intensive

study. To be presented at the AAAR meeting in Pittsburg, PA, March, 2003.

Shauer, J. J., Baie, M. S., Turner, J. R., White, W. .H., Koutrakis, P., Ondov, J. M., Pancras, J. P. (2003) New Insights into the dynamics of Sources of Fine Particulate Matter Using semi-continuous Chemical Speciation Samplers. Presented at the Association of Aerosol Research meeting, Particulate Matter: Atmosopheric Sciences, Exposure, and the Fourth Colloquium on PM and Human Health, March, Pittsburgh.

Turner, J. R., Allen, G., Bahadori, Chow, J. C, Hansen, D. A., Husar, R. B., Koutrakis, P., McMurry, P. H., Ondov, J. M., Schauer, J. J.,Watson, J. G.,, Weber, R. J. White, W. H., (2003). Overview of the Saint Louis Midwest Supersite. Presented at the Association of Aerosol Research meeting, Particulate Matter: Atmosopheric Sciences, Exposure, and the Fourth Colloquium onPM and Human Health, March, Pittsburgh.

Park, S. S., Harrison, D., Ondov, J. M., Tolocka, M. P., Lake, D. A., Johnston, M. V. (2003) Transient Elevations in the Concentrations of Sulfate, Nitrate, and EC/OC Measured with Semicontinuous Monitors at the Baltimore Supersite. Presented at the Association of Aerosol Research meeting, Particulate Matter: Atmosopheric Sciences, Exposure, and the Fourth Colloquium onPM and Human Health, March, Pittsburgh.

Ondov, J. M., Buckley, T. J., Hopke, P. K., Johnston, M. V. Parlange, M., Rogge, W., Squibb, K. S., Wexler, A. S. (2003). The Baltimore Supersite Project: Highly Time and Size Resolved Concentrations of Urban PM2.5 and its Constituents for Resolution of Immune Responses. Presented at the Association of Aerosol Research meeting, Particulate Matter: Atmospheric Sciences, Exposure, and the Fourth Colloquium on PM and Human Health, March, Pittsburgh.

Nair, N. P. V., Ondov, J. M., Park, S. S. (2003). Statistical Summary and Observations of Semicontinuous Particle Size Distributions Measured at the Baltimore Supersite. Presented at the Association of Aerosol Research meeting, Particulate Matter: Atmospheric Sciences, Exposure, and the Fourth Colloquium onPM and Human Health, March, Pittsburgh.

Ondov, J. M., Pancras, J. P., Gazula, S., Yu, M. N. S., Turner, J., Robinson, A., Pandis, S., Stevens, R. K., Poor (2003). Highly Time-Resolved Measurements of Elemental Composition at the Baltimore, St. Louis, Pittsburgh, and Tampa Supersites Using the UM High-Frequency Aerosol Slurry Sampler: Unprecedented Resolution of the Sources of Primary Atmospheric Aerosol. Presented at the Association of Aerosol Research meeting, Particulate Matter: Atmospheric Sciences, Exposure, and the Fourth Colloquium onPM and Human Health, March, Pittsburg.

Emily Wietkamp, Eric Lipsky, Allen Robinson, Natalie Anderson, Heather Leifeste, R. Subramanian, Juan Cabada-Amaya, Andrey Khlystov, Charles Stanier, Leonard Lucas, Satoshi Takahama, Beth Wittig, Cliff Davidson,, Spyros Pandis, Andrea Polidori, Ho-Jin Lim, Barbara Turpin, Patrick Pancras, John Ondov (2003) Fenceline sampling adjacent to a large coke production facility in Pittsburgh, PA Presented at the Association of Aerosol Research meeting, Particulate Matter: Atmospheric Sciences, Exposure, and the Fourth Colloquium on PM and Human Health, March, Pittsburgh.

FUTURE ACTIVITIES

1. We will continue to hold weekly PI teleconferences as needed.

2. We will continue to reduce and validate our data.

3. We will present the above listed presentations at the March 2003 AAAR PM meeting.

4. Additional DRUM, Sequential Organic, and SEAS samples will be selected for retrospective analyses.

5. We will complete data flagging and Level II QA activities and transfer data to NARSTO, anticipated completion: before March 25, 2003.

6. Several manuscripts are being prepared.

7. Clarkson University will classify the Supersites Data files for entry into the Supersites Relational Database.